PATENT SPECIFICATION

NO DRAWINGS

1.007.481

1,007,481

Date of Application and filing Complete Specification July 10, 1962.

No. 26456/62.

Application made in United States of America (No. 128963) on Aug. 3, 1961.

Complete Specification Published Oct. 13, 1965.

Index at acceptance:—C1 A(D41, G12, G44, G50); AG12D41, AG44D41, AG50D41; A5 E2; B2 B(4E1A1, 4E1A2, 4E1BY, 4E1C1, 4E3C, 4E5C, 4E7A3, 4E7AY, 4E7B1, 4E7B2, 4E7B4, 4E7B5, 4E7B6, 4E7BX, 4E8D, 4E8G, 4E9D, 4E9H, 4E9J, 4E9K, 4E9N, 4E9P); B5 N(2G, 2K4, 5C, 12); C3 N(3A2A, 3A3E, 3A3G, 3B4A, 3B9A, 3C, 6, 7, 12, 15); C3 P(2A, 2C4A, 2C4B, 2C8B, 2C14A, 2D1B, 2K7, 4A, 4C4A, 4C4B, 4C8B, 4C14A, 4D3B1, 10A, 10C4A, 10C4B, 10C8B, 10C14A, 10D1A); C4 A9A; C4 X5; C7 U(4A, 4B, 4C, 4H1, 4J, 4P, 7C); D1 P(3C, 3E, 3F2, 3G5); D1 R3; D2 B(2A, 2B, 14X)

Int. Cl.:—C 01 b//B 29d, B 44 d, C 08 f, g, C 09 d, j, k, C 23 f, D 04 j, D 06 m, D 21 h

COMPLETE SPECIFICATION

Compositions Containing Lithium and Sodium Silicates

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is directed to a single-application inorganic coating. More particularly, the invention is concerned with a liquid treating composition comprising a lithium silicate solution, which also contains sodium silicate and the application of this solution alone or with specific additives to numerous materials as a protective, bonding, and fire-resistant coating.

The solution of the present invention when used alone may be applied by brush, spray or dipping to materials, such as paper or fabric, and renders these materials non-flammable and moisture resistant. Materials which are rigid can be sealed against the passage of moisture and made fireproof by the solution of the present invention. Also, the solution of the present invention can be colored with stable dyes to impart desirable colors. When applied to either a flexible or rigid material, the solution of the present invention impregnates the material with a protective coating to a greater extent than known silicate solutions having comparable molar concentration because of the lower viscosity of the solution of the present invention. The protective coating is strong, moisture resistant, fire resistant, and has a low porosity. The protective nature of the coating has been found effective not only against water and fire, but provides protection from such things as abrasion, wear, weather, high temperatures and biological decomposition. The solution when applied to a material dries rapidly and when dried, surprisingly results in an insoluble coating.

The solution of the present invention is also capable of lending strength to wood as well as protection against rot, fire, water absorption, and may also be effective against termites, wood borers and other destructive insects. Further, the solution of the present invention is capable of bonding, waterproofing and general strengthening of glass matting, asbestos, paper or cloth and cellulosic materials generally. The solution may be sprayed, brushed, rolled or mopped on surfaces such as paper or generally applied to a surface of such a nature which may be impregnated with the solution. Still further, the solution of the present invention has been found to be a new and useful surface bonding, adhesive and cementing agent.

The present invention is still further directed to a single-application coating material wherein the solution of the present invention is used as a liquid vehicle to which is mixed inert fillers such as asbestos, dyes and/or colored pigments, together with emulsified polymers such as vinyl acetate, vinyl chlorate and butyl rubber. The coating of the present invention which incorporates the poly-

mers and inert fillers and pigments is suitable for coating metal, concrete, brick or plaster. The resulting coating is inexpensive, nonflammable, odorless and easy to apply by brush, roller or spray. The resulting film imparts color, corrosion protection, and seals the surface against the passage of moisture. The alkaline nature of the concrete or plaster, does not affect the coating's durability nor its ability to provide a water resistant protective coating. Thus, the protective coating of the present invention has application in coating concrete piping, coloring and sealing concrete blocks, plaster and bricks, marking highways, runways and parking areas, protection of metal surfaces, decorative coating for concrete floors, and general maintenance painting.

Surprisingly, it has been found that the incorporation of a dispersion of metallic dust in the silicate solution of the present invention, the silicate solution being used as a liquid vehicle, with a small but effective amount of an alkali metal dichromate provides a useful and important protective coating for metallic surfaces such as storage tanks for crude petroleum and fractions thereof such as gasoline, kerosene, gas oil, Diesel oil or heating and lubricating oils. The coating composition may also be employed to protect ships' bottoms and the interior of ships and tanks, providing protection from corrosion without contamination of hydrocarbons or aqueous solutions contained in the tanks.

The present invention is also concerned with a method of preparing the lithium-sodium silicate solutions in which lithium hydroxide, which is preferably the monohydrate since it is easier to use and gives an improved coating, silica-containing materials, such as silicic acid and silica gel and sodium hydroxide are added to water while agitating same, following which the mixture is heated while continuing the agitation thereof to a temperature within the range from 75° to 250°C, over a sufficient length of time to form the silicate, the sodium and lithium hydroxide and silica-containing material being used in amounts sufficient to provide a molar ratio of lithium oxide to sodium oxide to silicon dioxide within the range from 0.75 to 1.00:0.05 to 0.25:2.5 to 5.0, respectively. The admixture is then cooled to a temperature within the range from 20° to 30°C. at which temperature any solids go into solution and form an aqueous solution thereof. These dissolved solids, being dissolved lithium and sodium silicates, are preferably present in a combined amount by weight of from 10 to 45%, and more particularly of 24 to 31%, based on the weight of the aqueous solution.

Surprisingly, it has been found that the solution of the present invention, either used alone or in admixture with various additives, is an effective bonding, adhesive, and cementing agent. In this respect, the solution of the present invention is useful in bonding of two or more surfaces to produce a strong water resistant bond. In particular, the solution may be used in a large variety of surfaces such as: wood, paper, cardboard, cloth, plastics, glass, metals, concrete or brick. The solution of the present invention is, therefore, useful in the manufacture of items such as: corrugated paper boxes, ply wood, laminated fiber board, plastics, wall board, insulating board, sound-absorbing wall covering, laminated mica, refractory cements, grinding wheel abrasive surfaces, granular roof surface construction material, cement, mortar and acid resistant cements.

The bonding adhesive and cementing characteristics of the present invention may be improved by the addition of fillers selected from the group comprising casein, clay, sugars, aluminates and asbestos, as well as curing agents selected from the group comprising potassium chloride, potassium bromide or borax. These additives are added in amounts between 5% and 80% by weight, the fillers being used in an amount between 5% and 80% by weight and the curing agent in 0.01% to 3.0% by weight of the mixed composition. A preferred adhesive agent is adding to the lithium sodium silicate solution of the present invention 5 to 20% by weight of clay as a filler and 0.2% of borax as a curing agent.

One aspect of the present invention is the making and use of a lithium-sodium silicate solution without the addition of any additive materials. A composition in accordance with this aspect of the invention was made up in the following manner:

EXAMPLE 1

1146 gms water, 300 gms silica gel, 62 gms lithium hydroxide, and 20 gms sodium hydroxide were charged into a stainless steel pressure vessel equipped with an agitator. During the initial mixing of these ingredients, evolution of heat raised the temperature of the contents to 50°—55°C. The reactor was then sealed and the temperature of the reactants, under continual agitation, was raised to 150°C. over a period of time, which may vary from thirty to ninety minutes. After the vessel reached 150°C. and 70 pounds per square inch of pressure, the contents were slowly cooled at a rate of 0.61°C. to 1.83°C. per minute. This will resulted in a temperature drop from 150°C. to 95°C. within thirty to ninety minutes. This completed the initial part of the reaction which formed the solid sodium-lithium silicate.

The second part of the operation (below 95°C.) required a longer period of time in order to effectively dissolve the solid silicate

at lower temperatures. The reduction of the temperature of the reactor contents from 95°C. to 40°C. at a rate of 0.37°C. to 0.146°C. per minute was accomplished within 150 minutes to 240 minutes. The last temperature drop from 40°C. to 25°C. may be conducted over a period of 60 to 120 minutes at a cooling rate of 0.25°C. to 0.125°C. per minute.

Depending upon the amount of water used, the solution may be used in different solids ratios, i.e., the total solids of the solution may vary from 10% to 45% by weight.

Example 2

A solution was prepared exactly as described in Example 1 from the following ingredients:

Sodium Hydroxide	20 grams
Lithium Hydroxide Monohydrate	62 grams
Silica Gel	300 grams
Water	1146 grams

This solution can be described as $(0.75\ Li_2O + 0.25\ Na_2O):5\ SiO_2$ with a total solids content of about 25%. Cloth fabric and paper were saturated with this aqueous solution and allowed to air dry. After drying they were rigid, fireproof, and withstood 72 hours exposure to 100% relative humidity at 40°C.

Example 3

A solution identical to Example 2 was used as an adhesive binder for asbestos. The resulting composition was moisture resistant and fireproof. The composition was heated under an open flame for 3 hours and then inserted directly into cold water without affecting the cohesion of the material.

Example 4

A solution from Example 2 was used to seal preformed asbestos insulation against the passage of moisture. The solution was colored with a stable red dye in order to produce a colored seal coating. After 120 hours exposure to 100% relative humidity at 40°C., the solution exhibited excellent waterproofing properties.

The resulting lithium-sodium silicate composition of the present invention is moisture resistant and fireproof when applied by brush, spray or dipping to paper, fabric, cardboard, wallboard and similar materials. The solution of the present invention is prepared having a total solids content of between 10% and 45% by weight for the foregoing purposes.

Example 5

Liquid compound and preparation

Lithium Hydroxide monohydrate	62.0 grams
Sodium Hydroxide	20.0 grams
Silica Gel	270.0 grams
Water	952.0 grams

These chemicals were placed into a stainless steel pressure vessel under continual agitation. The temperature was raised to 150°C.; then the temperature was gradually reduced to 25°C. over an eight hour period in a manner similar to Example 1. A mixture containing 500.0 grams of this compound and 100.0 grams of water was placed into a container and three types of wood (pine, oak, fir) were immersed for 30 minutes under a constant pressure of 25 mm/Hg. The wooden panels were removed and dried thoroughly, then subjected to an open flame. The wood was charred but at no time did it burn. Amic roscopic examination revealed that approximately 60% of the voids in the wood were occupied by silica.

The solution of the present invention is capable of lending strength to wood as well as protection against rot, fire, and water absorption.

The solution of the present invention rather than being applied as a film may be applied by mixing the lithium-sodium silicate solution in a matrix such as glass fibers, asbestos, paper fibers or saw dust, and applied to a material as a protective coating directly by trowel. When mixed in a matrix of material the solution of the present invention has a solids content of 10% to 35% by weight. It has been found that the solution of the present invention whether applied as a film or mixed in a matrix is completely water insoluble when cured and is unaffected by most chemicals with the exception of hydrogen fluoride and strong concentrated alkalies. The effectiveness of the nonflammable, odorless, nontoxic solution is shown by the following examples:

Example 6

Lithium Hydroxide Monohydrate	62.0 grams
Sodium Hydroxide	20.0 grams
Silica gel	270.0 grams
Water	952.0 grams

These chemicals were placed into a stainless steel pressure vessel under continual agitation. The temperature was raised to 150°C.; then the temperature was gradually reduced to 25°C. over an 8 hour period in a manner similar to Example 1.

Example 7

1. Solution of Example 6—25% Solids
2. 30 oz. glass matting

The glass matting was dipped in the solution and allowed to air dry at 25°C. for 2 hours. The matting was then subjected to elevated temperatures and exhibited rigidity and superior binding qualities at temperatures nearing the melting point of glass.

Example 8

1. Solution of Example 6—25% Solids
2. Asbestos

The solution was mixed with asbestos fibers and applied by brush to a sandblasted furnace stack at approximately 90°C. The asbestos and lithium-sodium silicate solution exhibited excellent adhesion and good insulative qualities.

EXAMPLE 9

1. Solution of Example 6—25% Solids
2. Paper Fibers

The paper fibers were dispersed in the solution and applied by hand to a steam line exposed to the weather. After 60 days exposure there was no visible deterioration and excellent adhesion as well as insulative qualities were observed.

Another unique feature of the present invention is that the lithium-sodium-silicate solution may be used as a surface bonding, adhesive, and cementing agent.

It has been found that the mixed lithium-sodium silicate solution of the present invention, when applied to a surface and allowed to dry, has a much smaller porosity than known silicate solutions, and hence, the bonding, adhesive, and cementing characteristics of the present invention are greater than other known silicates.

The following examples are given as illustrations of the bonding, adhesive and cementing characteristics of the present invention.

EXAMPLE 10

The lithium-sodium silicate solution, identical in composition to that described in Example 2, was applied to the surface of two pieces of ordinary, brown cardboard. The two pieces of cardboard were then pressed together and held under pressure in a vise and allowed to dry for 24 hours. The resulting bonding was excellent as evidenced by the fact that upon pulling the two pieces apart, the paper fibers were pulled apart rather than a separation occurring at the original interface.

EXAMPLE 11

In another experiment, an adhesive mixture was prepared by thoroughly mixing 80 parts of the lithium-sodium silicate solution of Example 2 with 20 parts of dry powdered clay. A small double layer piece of cheese cloth was dipped into this mixture and placed between two pieces of brown paper and pressed together in a vise for a period of two hours. The sample was then removed and allowed to dry for an additional hour. The resulting bonding was stronger than the paper itself.

Another aspect of the present invention is a water based coating which will dry by water evaporation into a water and hydrocarbon resistant film composition for metal, concrete, brick or plaster which are of such a nature as to be impregnated with the coating. The coating is obtained by using the lithium-sodium silicate solution of the present invention as a liquid vehicle and adding thereto a mixture of inert fillers such as asbestos, dyes and/or colored pigments together with emulsified polymers such as polyvinyl acetate, polyvinyl chlorate and butyl rubber. The best general coating composition illustrating this aspect of the invention can be described by the general formula A (Polymer)+B[(CLi_2O+DNa_2O) : E SIO_2] wherein the coefficients A, B, C, D and E have the following numerical values:

A=50 to 100 parts by weight
B=5 to 50 parts by weight
C=0.75 to 1.0 moles
D=0.05 to 0.25 moles
E=2.5 to 5.0 moles

Further, the concentration of the coating composition should be such that the total solids of the composition should be 30%—40% by weight. The advantages of a coating having the polymers incorporated therein are shown by the following specific examples:

EXAMPLE 12

Lithium-Sodium Silicate Vehicle

Lithium Hydroxide monohydrate	62.0 grams
Sodium Hydroxide	20.0 grams
Silica Gel	270.0 grams
Water	952.0 grams

These ingredients were placed into a stainless steel pressure vessel under continual agitation. The temperature was raised to 150°C.; then the temperature was gradually reduced to 25°C. over a period of 8 hours in a manner similar to Example 1.

Polyvinyl Acetate Component

Vinyl Acetate	43.75 grams
2-ethylhexyl acrylate	6.25 grams
Water	70.00 grams
A commercial alkyl phenyl ether of polyethylene glycol emulsifier	0.75 grams
A commercial hydroxyethyl cellulose protective colloid	1.00 grams
Potassium Persulfate	0.18 grams

The colloid, emulsifier and potassium persulfate, used as a catalyst, were blended into the water in a polymerization reactor equipped with an agitator and a condenser. The vinyl acetate and 2-ethylhexyl acrylate were combined and 10% by weight was added to the aqueous system. The aqueous system was warmed to 70°C. with agitation. The remaining vinyl acetate and 2-ethylhexyl acrylate mixture was added with stirring over a three-hour period maintaining the temperature of the reaction at 70—80°C. After the addition was complete, agitation was continued for one-half hour. The contents were then cooled to room temperature.

Coating Composition

Lithium-Sodium Silicate Vehicle	500 grams
Polyvinyl Acetate Emulsion	500 grams
Iron Oxide	50 grams
Inert Talc filler	200 grams

The iron oxide and talc were dispersed in the vinyl acetate emulsion and the silicate solution was then added. The coating mixture was applied over ferrous metal surfaces which had been wire brushed. Upon drying by water evaporation, the coating exhibited excellent adhesion, hardness and moisture resistance. It had an initial gloss of 30 as determined by a 60° gloss meter, withstood a 1/8 inch mandrel bend for flexibility and 8000 scrub cycles in a 5% soap solution. (ASTM D-16) The coating was not affected after 96 hours exposure to 100% relative humidity at 40°C.

Corparative Test (A)

A coating composition was prepared in the same manner as described in Example 12 except it had the following composition:

A (Polyvinyl Acetate Emulsion3+B
$[(C\ Li_2O+D\ Na_2O):E\ Si_2O]$

A=100 parts
B= 0 parts
C= 0 parts
D= 0 parts
E= 0 parts

Coating Composition

Polyvinyl Acetate	1000 grams
Iron Oxide	50 grams
Inert Talc filler	200 grams

This coating had poor adhesion and hardness. It exhibited blistering after 96 hours exposure to 100% relative humidity at 40°C. It withstood only 350 scrub cycles.

EXAMPLE 13

Another coating composition was prepared in the same manner as described in Example 12 except it had the following composition:

A (Polyvinyl Acetate Emulsion)+B
$[(C\ Li_2O+D\ Na_2O):E\ Si_2O]$

A= 0 parts
B=100 parts
C= 0.75 mol
D= 0.25 mol
E= 4.5 moles

Coating Composition

Lithium-Sodium Silicate Vehicle	1000 grams
Iron Oxide	50 grams
Inert Talc Filler	200 grams

This coating was not completely satisfactory in that it became very brittle and flaked from the surface. Further, it failed to produce a continuous film. Although brittle, it exhibited excellent water insoluble properties.

EXAMPLE 14

Butyl rubber latex was pigmented and applied to a steel panel where it air dried with some corrosion of the steel. It had very poor adhesion and hardness. However, the addition of the lithium-sodium silicate as shown in the following table resulted in a film that was superior in adhesion, hardness and flexibility.

Coating Composition

Lithium-Sodium Silicate Vehicle	250 grams
Butyl Rubber Latex 54% Solids	1000 grams
Water	100 grams
Talc-inert filler	200 grams
Iron Oxide	50 grams

Another important aspect of the present invention is to form a dispersion of metallic dust in the aqueous lithium-sodium silicate solution of the present invention. It has been found that the dispersion of a metallic dust, such as zinc, in the aqueous solution of the present invention, used as a liquid vehicle, and a small but effective amount of an alkali metal dichromate provides a useful coating for protecting metallic surfaces. Surprisingly, the coating provides protection from corrosion without contamination of hydrocarbons or aqueous solutions, which may be in contact with the coated surfaces. A composition representing this aspect of the present invention is made in the same manner as described in Example 1 except that after the solution has cooled, a small but effective amount of an alkali metal dichromate, such as sodium or potassium dichromate, is added. A finely divided metal, such as zinc dust, is then added to the cooled solution in sufficient amounts to provide a protective surface when the composition is to be applied to exposed surfaces. Optionally, there may be added to the cooled solution prior to, or simultaneously with the zinc dust an alkaline metal borate, iron oxide, or sodium bicarbonate, if desired, which improve the characteristics of the protective metal coating when the solution is applied to an exposed surface.

The finely divided metal is preferably zinc dust having a particle size within the range from 3 to 25 microns; however, a preferred particle size is within the range from 6 to 10 microns. With the zinc dust may be used other metallic dusts, such as aluminium dust, magnesium dust, and selected metal oxide dust such as manganese dioxide, titanium dioxide or iron oxide. It is preferred, however, that when other metallic ingredients are employed that the zinc dust be used in a major amount. Other materials such as sand and silica gel may be additionally employed, but it is to be emphasized that zinc dust is preferably employed in a major amount when the composition is used as a coating for protecting metallic surfaces. It

has been found that when a small but effective amount of the metal oxides is used that this improves abrasion resistance, resistance to boiling water and hot salt water spray and also improves the over-all general appearance of the metallic coating when applied to exposed surfaces.

A preferred ratio of the mixture when a metallic dust is added is 0.8 of lithium oxide: 0.2 of sodium oxide: 4.5 of silicon dioxide. The total weight per cent of the lithium hydroxide and sodium hydroxide in the solution having a metallic dust may range from 5.0 to 15.0 per cent. The amount of silica gel or silicic acid used to prepare the silicates may range from 8 to 25 per cent by weight based on the total weight of the composition.

The presence of an alkali metal borate, such as sodium borate or potassium borate, or ammonium borate, greatly reduces or eliminates the friability of the final coating and allows the provision of a thicker coat than otherwise might be obtained. An amount of the borate in the range from 0.01 to 0.20 per cent by weight of the total composition may be used. Thus, single-application compositions wherein the borate is not present and used to provide coatings having a thickness not greater than from 3 mils to 6 mils, may have surface cracks rendering the coatings unsuitable. Where a borate is present in the amount above stated, however, a coating of at least 18 mils thickness may be obtained with no signs of surface cracking.

Also, when using metallic dust in the solution of the present invention, it is desirable to employ an alkali metal bicarbonate, such as sodium bicarbonate or ammonium bicarbonate. The presence of this material improves the water insolubility and accelerates the "self-curing" or "air-curing" characteristics of the coating. Where a bicarbonate is employed, it may be present in an amount in the range from 0.01 to 0.20 per cent by weight based on the total weight of the composition.

An important feature of the present invention when preparing a coating for a metallic surface is the presence of an oxidizing agent, such as an alkali metal dichromate as exemplified by potassium dichromate or sodium dichromate. The presence of the oxidizing agent increases the useable or pot life of the coating material after metal dust and the liquid vehicle have been admixed. For example, by dissolving 0.05 to 0.10 per cent by weight of potassium dichromate in the liquid vehicle, the useful life of the coating mixture is substantially lengthened.

Example 15

A stainless steel autoclave suitably equipped with a stirring device and capable of withstanding an internal autogenous pressure of at least 600 psi, and equipped with a heating device such that the contents may be heated to about 250°C. was provided. The autoclave was charged with 400 parts by weight of water and the stirring device was placed in operation. About 34 parts of lithium hydroxide containing 1 molecule of water and 8 parts of sodium hydroxide were added to the water in the autoclave and stirred from 5 to 10 minutes. Thereafter, about 126 parts of silica gel were added. Silicic acid may be substituted for the silica gel, but it will be necessary to adjust the amount thereof because of the presence of the water of hydration. The autoclave was then closed and stirring was continued and it was then heated to a temperature within the range indicated, preferably 140° to 150°C. The temperature of the contents of the autoclave was brought up to the maximum temperature over a period of about 30 minutes, and thereafter the temperature was slowly reduced to a temperature of 20° to 30°C., preferably 25°C., over a period up to 6 hours. Stirring was then continued for an additional period of time up to 14 hours, at which time there was added to the contents of the autoclave 0.05 per cent by weight of an alkaline dichromate in the form of potassium dichromate. An alkali metal borate, such as sodium borate, in an amount of 0.02 per cent by weight and an alkali metal bicarbonate, such as sodium bicarbonate in an amount of about 0.15 per cent by weight may also be added. Stirring was continued until a complete solution was effected, which may be for about 10 minutes. This provided a single-application coating composition, and the composition was suitable for immediate use. To the liquid composition was then added 300 parts of zinc dust for every 100 parts of the composition as described above. This composition may then be applied to a freshly sandblasted surface, such as a metallic surface as exemplified by steel, and allowed to dry by exposure to the atmosphere for about one hour.

Comparative Test (B)

Sodium silicate was employed in this composition in a molar ratio of 3.22 of silicon dioxide to sodium oxide at 30 per cent solids by weight employing 0.05 per cent potassium dichromate. This aqueous solution was mixed at a 3:1 weight ratio using zinc dust having a particle size of 10 to 12 microns. When this composition was applied to a sandblasted steel panel and allowed to air dry one hour and then exposed to boiling water for 5 minutes, the coating was completely destroyed.

Comparative Test (C)

In another composition, a molar ratio of 4.5:1 of silicon dioxide to lithium oxide was employed at 26—27 per cent solids by weight

and the aqueous solution mixed at a 3:1 weight ratio using zinc dust having a particle size of 10 to 12 microns. Application of this composition to a sandblasted steel panel indicates unsatisfactory results when allowed to dry in air one hour and then exposed to boiling water for one hour. That is, the coating is insoluble but exhibits excessive friability. The initial hardness of the coating is inadequate. A similar composition is also made, except that zinc dust having a particle size of 3 to 5 microns is employed. In the same test, the coating is found insoluble, but exhibits friability. The initial hardness of the coating is adequate, but the film thickness is insufficient in that surface or mud cracking is observed.

EXAMPLE 16

Thereafter, a composition in accordance with the present invention was made wherein silicon dioxide to total lithium and sodium oxides in a molar ratio of 4.5:1.0 was prepared. In this instance, the ratio of lithium oxide to sodium oxide was 3:1. Potassium dichromate in an amount of 0.05 per cent by weight of the aqueous solution was mixed with zinc dust, the zinc being employed in a ratio of 3 parts zinc to 1 part of solution. The resulting composition was applied to a sandblasted steel panel and allowed to dry in air for one hour and then exposed to boiling water for one hour. This composition exhibited unusual water insolubility and no friability was observed. Moreover, the initial hardness of the coating was greater than the corresponding lithium silicate composition.

EXAMPLE 17

Another composition wherein silicon dioxide to total lithium and sodium oxides in a molar ratio of 4.5 to 1.0 was prepared. In this instance, the ratio of lithium oxide to sodium oxide was 4:1. Potassium dichromate in an amount of 0.05 per cent by weight was mixed with the alkali metal silicate solution. The zinc dust, having an average particle size of 7 to 9 microns, was employed in a ratio of 3 parts of zinc to 1 part of solution. The resulting composition was applied to a sandblasted steel surface and allowed to air dry for one hour, then exposed to boiling water for one hour. The composition exhibited unusual water insolubility and no friability was observed. The initial hardness of the coating was 8H, as determined by standard pencils, and it withstood 5 to 6 per cent elongation upon being impacted with a force of 13.4 foot pounds. Also, the resulting coating withstood one thousand hours exposure to 5% warm salt spray and one thousand hours exposure to 100 per cent relative humidity at 40°C. without failure. The abrasion resistance of the coating, as determined by a Taber abraser, was outstanding and required 10,000 cycles to destroy 1 mil thickness of the coating. Adequate film thickness of 12—14 mils could be applied without surface cracking.

EXAMPLE 18

The same composition was again prepared as in Example 17 except that zinc dust having a particle size of 10—12 microns was employed. The resulting coating after air drying one hour exhibited the same unsual water insolubility, but had a soft, less abrasive resistant film. Only 6000 cycles on the Taber abraser was required to destroy one mil thickness of the film and the pencil hardness was 6H+. However, 15 to 20 mil film thicknesses could be applied without surface cracking and flaking of the coating.

EXAMPLE 19

Another composition wherein silicon dioxide to total lithium and sodium oxides in a molar ratio of 4.5:1.0, was prepared. In this instance, the ratio of lithium oxide to sodium oxide was 1:1. Potassium dichromate in an amount of 0.05 per cent by weight was mixed with the alkali metal silicate solution. The zinc dust having an average particle size of 7 to 9 microns was employed in a ratio of 3 parts of zinc to 1 part of solution. The resulting composition was applied to a sandblasted steel surface and allowed to air dry for one hour, then exposed to boiling water for 30 minutes at which time, the coating was destroyed. The initial hardness of the coating was 8H+ and withstood 5 to 6 per cent elongation upon being impacted with a force of 13.4 foot pounds. Also, the resulting coating exhibited 80 per cent failure after being exposed for only one hundred and fifty hours in 5% warm salt spray and 80% failure after exposure of three hundred hours to 100% relative humidity at 40°C. However, thick films of 20 mils could be applied without surface cracking.

EXAMPLE 20

Another composition wherein silicon dioxide to total lithium and sodium oxides in a molar ratio of 4.5 to 1.0, was prepared. In this composition, the ratio of lithium oxide to sodium oxide was 9:1. Potassium dichromate in an amount of 0.05 per cent by weight was mixed with the alkali metal silicate solution. The zinc dust having an average particle size of 10 to 12 microns was employed in a ratio of 3 parts of zinc to 1 part solution. The resulting composition was applied to a sandblasted steel surface and allowed to air dry for one hour, then exposed to boiling water for one hour. The composition exhibited good water insolubility and very slight friability. The

initial hardness of the coating was 6H and it withstood 5 to 6 per cent elongation upon being impacted with a force of 13.4 foot pounds. It passed a one-half inch mandrel bend for flexibility, but required only 6000 cycles on the Taber abraser to destroy one mil of coating thickness. Films of 15 to 16 mils could be applied without surface cracking or flaking of the coating.

EXAMPLE 21

The same composition was again prepared as in Example 20 except that zinc dust having a particle size of 7 to 9 microns was employed. The resulting coating after air drying one hour exhibited unusual water insolubility and excellent initial hardness of 6H+. Eight thousand cycles on the Taber abraser was required to destroy one mil of coating film, and it withstood 5 to 6 per cent elongation upon being impacted with a force of 13.4 foot pounds. Adequate film thickness of 10 to 12 mils can be applied without surface cracking and flaking.

In the foregoing compositions, reference is had to solids content. In the practice of the present invention, the total solids dissolved in the liquid composition should be in the range of 10 to 45, and preferably 24 to 31 per cent by weight as determined by heating a weighed quantity of the liquid composition at 110°C. to dryness and then weighing to determine the per cent of solids.

EXAMPLE 22

A liquid composition in accordance with this embodiment of the present invention which is exclusive of the metallic dust and other additives, but which contained potassium dichromate, was made up of the following:

Components	Pounds
Sodium hydroxide	3.75
Lithium hydroxide monohydrate	11.75
Silica gel	50.50
Water	178.00
Potassium dichromate	0.122
	244.122

The several components, excepting the potassium dichromate, were charged, in the order shown, into a stainless steel pressure vessel equipped with an agitator. The mixture increased in temperature from 25°C. to 50°C. by evolution of exothermic heat. The vessel was then sealed and the temperature and pressure of the contents under continual agitation were raised to 150°C. and 60 pounds per square inch within 30 minutes. When the temperature reached 150°C., the contents of the vessel were slowly cooled at an average rate of 0.347°C. per minute which resulted in a temperature drop from 150°C. to 25°C. in 360 minutes. The pressure vessel was then opened and the potassium dichromate was added to the solution under vigorous agitation. When all of the chromate was completely dissolved, the finished lithium-sodium silicate was withdrawn from the vessel.

In employing the present invention, a useful protective coating mixture is provided by mixing a finely divided metal, such as a mixture of zinc or aluminium dust, with alkali metal dichromate and optional ingredients with a liquid composition containing lithium and sodium silicates in a weight ratio of 2:1 to 4:1 of a metallic dust to liquid vehicle. The coating mixture is applied to a freshly sandblasted metal surface, such as steel or other metals, by spray, brush, roller or dipping and allowed to dry in the air. The resulting coating is abrasive resistant, withstands the action of boiling water for eight hours, withstands hot salt water spray for several weeks, and provides a superior coating composition. In testing the steel panels, the coating was sprayed on a freshly sandblasted piece of 1/8-inch thick steel plate four inch wide and four inches long. The test panels on which the coating was sprayed were air dried at about 25°C. for one hour and then subjected to physical testing, such as immersion in boiling water, exposure to a 5 per cent heated salt-water spray for periods up to one thousand hours, exposure to 100 per cent relative humidity at a temperature of 38° to 40°C. for a period of one thousand hours and exposure to hot liquid hydrocarbons. The hardness of the coating was determined by the use of standard pencils of various hardness ratings. Abrasion resistance was also employed as an indication of the hardness of the coating as determined by the Taber abraser with a CS-17 abrading wheel and 1000 gram load. Flexibility was determined by a 90° bend of a test panel on which the coating was applied and by impact of a coated panel with a force of 13.4 foot pounds.

In our co-pending Application 1007482, No. 12531/65 we have described and claimed aqueous solutions of lithium silicate wherein the molar ratio of lithium oxide to silicon oxide is within the range of 1:2 to 1:6.3.

WHAT WE CLAIM IS:—

1. A composition comprising an aqueous solution of lithium silicate and sodium silicate said lithium silicate and said sodium silicate being present in amounts such as to provide a molar ratio of lithium oxide to sodium oxide to silicon dioxide in the range of from 0.75 to 1.0 of lithium oxide, from 0.05 to 0.25 of sodium oxide and from 2.5 to 5.0 of silicon dioxide.

2. A composition as claimed in claim 1 wherein the combined amount by weight of the said lithium silicate and the said sodium silicate, based on the weight of the aqueous solution is from 10 to 45%.

3. A composition as claimed in claim 1 wherein the combined amount by weight of the said lithium silicate and the said sodium silicate, based on the weight of the aqueous solution, is from 24 to 31%.

4. A composition as claimed in any of claims 1, 2 or 3 containing additionally a filling material selected from the group consisting of casein, clay, sugar, asbestos or an aluminate and a curing agent selected from the group consisting of borax, potassium chloride and potassium bromide.

5. A composition as claimed in claim 4 wherein the amount of the said filling material is from 5 to 80% by weight of the composition and the amount of the said curing agent is from 0.01 to 3.0% by weight of the composition.

6. A composition of matter as claimed in any of the preceding claims impregnated into wood, glass matting or cellulosic material.

7. A composition as claimed in any of the preceding claims containing additionally an emulsified polymer, iron oxide and talc.

8. A composition as claimed in claim 7 wherein the said emulsified polymer is emulsified polyvinyl chloride, polyvinyl acetate or butyl rubber.

9. A composition as claimed in any of the preceding claims containing a minor amount of an alkali metal dichromate.

10. A composition as claimed in claim 9 containing a dispersion of zinc dust.

11. A composition as claimed in claim 10 wherein the particle size of the said zinc dust is in the range of from 3 to 25 microns.

12. A composition as claimed in claim 10 wherein the particle size of the zinc dust is in the range of from 6 to 10, and preferably from 7 to 9, microns.

13. A composition as claimed in claims 10 to 12 containing a minor amount of an alkali metal or ammonium borate.

14. A composition as claimed in any of claims 10 to 13 containing three parts by weight of zinc dust to each part by weight of the said lithium and sodium silicates combined, the molar ratio of lithium oxide to sodium oxide in the said silicates being 3:1, the molar ratio of the silicon dioxide to the lithium oxide and sodium oxide together being 4.5:1 and potassium dichromate being present in an amount of 0.05% by weight of the weight of the aqueous solution.

15. A method of preparing an aqueous solution of lithium silicate and sodium silicate as claimed in claim 1 comprising mixing lithium hydroxide, sodium hydroxide, a silica-containing material selected from the group consisting of silica gel and silicic acid, and water, with agitation, heating said mixture whilst continuing the agitation thereof to a temperature within the range of 75 to 250°C. for a sufficient length of time to form an admixture of lithium and sodium silicates, said lithium and sodium hydroxides and silica-containing material being employed in amounts sufficient to provide a ratio of lithium oxide to sodium oxide to silicon dioxide in the range of from 0.75 to 1.0 of lithium oxide, 0.05 to 0.25 of sodium oxide and 2.5 to 5.0 of silicon dioxide, and cooling said admixture to a temperature in the range of from 20 to 30°C to produce an aqueous solution containing the said lithium and sodium silicates.

16. The method according to claim 15 wherein the total solids dissolved in the said solution is from 10 to 45%, and preferably from 24 to 31% by weight based on the weight of the said solution.

17. The method according to claim 15 or claim 16 wherein the said mixture is heated at a temperature of 150°C., the mixture then cooled to a temperature of about 95°C at a rate in the range of 0.61°C to 1.83°C per minute and then cooled to a temperature of 40°C at a rate in the range of 0.37 to 0.146°C per minute.

18. The method according to any of claims 15, 16 or 17 wherein there is added to the cooled solution a minor amount of an alkali metal dichromate.

19. The method according to claim 18 wherein there is added to the cooled solution a minor amount of zinc dust.

20. The method according to claim 19 in which there is added to the cooled solution a minor amount of an alkali metal or ammonium borate.

21. The method according to claim 19 or claim 20 wherein the particle size of the zinc dust is from 3 to 25 microns.

22. A composition as claimed in claim 1 substantially as described herein with particular reference to the Examples.

23. A method of preparing a composition as claimed in claim 15 substantially as described herein with particular reference to the Examples.

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Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1965.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.